

## THE NEAR INFRARED ABSORPTION SPECTRUM OF METHANE

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(Received November 12, 1931)

## ABSTRACT

The infrared absorption spectrum of methane between  $1.4\mu$  and  $2.6\mu$  was obtained with an infrared spectrometer having a grating of 5000 lines to the inch. Strong bands were found in the  $1.6\mu$  and  $2.3\mu$  regions. The fine structure of the  $2.3\mu$  band was resolved in the first order spectrum. The fine structure of the  $1.6\mu$  band was resolved in the second order but not in the first order spectrum. Only at the  $2.20\mu$  and the  $1.66\mu$  bands could the fine structure be measured. The  $2.20\mu$  band has spacing of  $10.7\text{ cm}^{-1}$ , giving for the value of the moment of inertia  $5.17 \times 10^{-40}$  c.g.s. units. The corresponding values for the  $1.66\mu$  band are  $10.4\text{ cm}^{-1}$  and  $5.32 \times 10^{-40}$  c.g.s. units. These results are quite close to the values of  $9.77\text{ cm}^{-1}$  and  $5.66 \times 10^{-40}$  c.g.s. units found for the  $3.31\mu$  band by Cooley.

## INTRODUCTION

COOLEY<sup>1</sup> has investigated the infrared absorption spectrum of methane. He resolved the rotational fine structure of the  $3.3\mu$  and the  $7.7\mu$  bands, but did not resolve the strong bands found in the  $2.3\mu$  region. Ellis<sup>2</sup> investigated the vibration bands of methane from  $1\mu$  to  $3\mu$  with apparatus of low dispersion. Easley, Fenner and Spence<sup>3</sup> found many bands between  $1\mu$  and  $3\mu$  in the spectra of the halogen derivatives of methane and ethane in the liquid form. It was thought worthwhile to investigate the absorption spectrum of methane in vapor form in the region from  $1\mu$  to  $3\mu$  with apparatus of high dispersion.

For a long time the model of the methane molecule almost universally accepted<sup>4</sup> was a regular tetrahedron with the carbon atom at the center and the four hydrogen atoms at the corners. More recently evidence has been brought forward in favor of a model in which the carbon atom forms the apex, and the four hydrogen atoms the base of a regular pyramid.<sup>5</sup> The fine structure of the bands measured by Cooley<sup>1</sup> at  $3.3\mu$ ,  $3.5\mu$ , and  $7.7\mu$  have different spacings. On the quantum theory, this indicates different moments of inertia about different axes. The conflicting evidence for and against a symmetrical model has attracted much attention to the structure of the methane molecule. Several solutions have been given in an attempt to describe its vibrational and rotational motions.<sup>6</sup>

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<sup>1</sup> Cooley, *Astrophys. J.* **62**, 73 (1925).

<sup>2</sup> Ellis, *Proc. Nat. Acad. Sci.* **13**, 202 (1927).

<sup>3</sup> Easley, Fenner and Spence, *Astrophys. J.* **67**, 3 (1928).

<sup>4</sup> Glockler, *J.A.C.S.* **48**, 2021 (1926). This summarizes the evidence in favor of the tetrahedral type of molecule.

<sup>5</sup> Henri, *Chem. Rev.* **4**, 189 (1927).

<sup>6</sup> Dennison, *Astrophys. J.* **62**, 84 (1925); Guillemin, *Ann. d. Physik* **81**, 176 (1926); Ruark and Urey, *Atoms, Molecules and Quanta*, p. 435 (1930).

## APPARATUS AND EXPERIMENTAL PROCEDURE

Radiation from the Nernst glower, passed through a Pyrex glass absorption cell 30 cm long, and was focused on the slit of an infrared grating spectrometer. The maximum slit width throughout the experiment was 0.025 cm. The grating of the spectrometer had a surface 16 cm long and 13 cm high ruled with 5000 lines per inch. The intensity of radiation of any particular wave-length was determined by a radiometer.<sup>7</sup> The slit width of 0.025 cm corresponded to wave-length interval of 12A. The smallest division on the dial of the spectrometer corresponded to approximately 10 angstroms.

TABLE I. *Methane 1.66 $\mu$  band region, second order.*

Quantum number	Spectrometer setting	Wave-length $\mu$	Frequency $\text{cm}^{-1}$	Frequency difference $\text{cm}^{-1}$
13	35.985	1.6292	6137.0	
12	36.04	1.6317	6128.0	9.
11	.10	1.6342	6119.0	9.
10	.145	1.6362	6111.6	7.4
9	.205	1.6388	6102.0	9.6
8	.265	1.6414	6092.2	9.8
7	.325	1.6441	6082.2	10.0
6	.39	1.6470	6071.6	10.6
5	.455	1.6498	6061.2	10.4
4	.505	1.6519	6053.4	7.8
3	.575	1.6550	6042.2	11.2
2	.65	1.6582	6030.4	11.8
1	.715	1.6611	6020.0	10.4
0	$2\nu_3$ .795	1.6645	6007.8	12.2
-2	.905	1.6692	5990.6	17.2
-3	.99	1.6729	5977.4	13.2
-4	37.06	1.6760	5966.4	11.0
-5	.13	1.6790	5956.0	10.4
-6	.205	1.6822	5944.4	11.6
-7	.28	1.6856	5932.4	12.0
-8	.35	1.6886	5921.8	10.6
-9	.445	1.6927	5907.6	14.2
-10	.52	1.6960	5896.2	11.4
-11	.59	1.6991	5885.2	11.0
-12	.64	1.7013	5877.8	7.4

The methane gas was generated by dropping water on magnesium carbide. The gas was then dried by passing it through a calcium chloride drying tube. Comparison was made with the water vapor bands described by Sleator and Phelps,<sup>8</sup> and with the bands of acetylene, ethylene, and ethane described by Levin and Meyer.<sup>9</sup> The bands found did not correspond to any of the gases named. Comparison of the bands with the results of Cooley<sup>1</sup> and Ellis<sup>2</sup> show conclusively that the bands described are all due to methane.

Readings in the important band regions were taken at intervals of about 10 angstroms. Readings were repeated over and over so that bands found are authentic beyond question. Most of the points of minimum transmission were read correctly to 5 angstroms or less.

<sup>7</sup> Spence, J.O.S.A. **6**, 625 (1922).

<sup>8</sup> Sleator and Phelps, *Astrophys. J.* **62**, 28 (1925).

<sup>9</sup> Levin and Meyer, J.O.S.A. **16**, 137 (1928).

Methane bands were found in the three regions,  $1.6\mu$ ,  $2.3\mu$ , and  $3.3\mu$ . The first two are of the first order spectrum, the third is a second order spectrum of the  $1.6\mu$  region. This conclusion was reached by the following reasoning: Pyrex glass transmits very effectively to  $2.5\mu$ ,<sup>10</sup> but the thickness used, 7 mm, would render it practically opaque to the radiation beyond that point. The radiation from the Nernst glower is very intense from  $1.2\mu$  to  $2.5\mu$  with a deep

 TABLE II. Methane  $2.2\mu$  band region.

Quantum number	Spectrometer setting	Wave-length	Frequency $\text{cm}^{-1}$	Frequency difference $\text{cm}^{-1}$
7	23.63	2.1600	4629.6	
6	.70	2.1663	4616.1	13.5
5	.767	2.1728	4602.3	13.8
4	.83	2.1780	4591.3	11.0
3	.88	2.1825	4581.0	10.3
2	.95	2.1888	4568.6	12.4
0 ( $\nu_2 + \nu_3$ )	24.07	2.1993	4547.0	21.6
-2	.19	2.2100	4524.9	22.1
-3	.25	2.2153	4514.0	10.1
-4	.30	2.2200	4504.5	9.5
-5	.365	2.2258	4492.8	11.7
-6	.42	2.2306	4483.1	9.7
-7	.48	2.2360	4472.3	10.8
-8	.53	2.2405	4463.3	9.0
-9	.59	2.2460	4452.4	10.9
( $\nu_4^+ + \nu_3^+$ )	.755	2.2608	4423.	
	.83	2.2678	4409.	
	.91	2.2750	4396.	
	.99	2.2820	4382.	
	25.06	2.2883	4370.	
	.11	2.2928	4361.	
	.17	2.2981	4351.	
	.21	2.3018	4344.	
( $\nu_4 + \nu_3$ )	.37	2.3162	4317.	
	.57	2.3342	4284.	
	.64	2.3407	4272.	
	.71	2.3470	4261.	
	.75	2.3505	4254.	
$\nu_1$	.97	2.3704	4219.	
	26.11	2.3829	4197.	
	.14	2.3857	4192.	
	.18	2.3892	4185.	
	.23	2.3935	4178.	
	.28	2.3980	4170.	
	.33	2.4025	4162.	
	.38	2.4068	4155.	
	.48	2.4158	4139.	
( $\nu_2 + 2\nu_4$ )	.57	2.4238	4126.	
	.70	2.4355	4106.	
	.78	2.4428	4094.	
	.83	2.4472	4086.	

minimum at  $3\mu$  to  $4.5\mu$ .<sup>11</sup> The second order of the  $1.6\mu$  region contains considerable energy, and lies in a region where the first order is cut off by the Pyrex glass. The bands of methane at  $1.6\mu$  and  $2.3\mu$  agree closely with those measured by Cooley and Ellis. The band at the  $3.3\mu$  region does not correspond

<sup>10</sup> Coblenz, Emerson and Long, U. S. Bur. Std. Bull. 14, 653 (1918).

<sup>11</sup> Coblenz, U. S. Bur. Std. Bull. 4, 533 (1908).

with those measured by Cooley, but has twice the wave-length of the band in the  $1.6\mu$  region. Similar consideration of the bands in the other compounds investigated make it certain that the bands at  $3.3\mu$  region are of the second order.

## RESULTS

Two groups of bands were found in the near infrared spectrum of methane, one in the region of  $1.6\mu$ , the other in the region of  $2.3\mu$ . The wave-lengths of the individual lines are shown in Tables I and II. The wave-

TABLE III. Methane band centers.

Designation	Moorhead		Frequency cm <sup>-1</sup>	Cooley		Ellis	
	Spectrometer setting	Wave-length $\mu$		Wave-length $\mu$	Wave-length $\mu$		
$3\nu_3$						1.15	
$\nu_4+2\nu_3$						1.37	
$2\nu_3$	18.16	1.6645	6008.			1.66	
	18.61	1.7055	5863.				
	18.84	1.7265	5785.			1.72	
						1.80	
$\nu_2+\nu_3$	24.07	2.1993	4547.	2.2008		2.20	
$\nu_4^++\nu_3^+$	.755	2.2608	4423.			2.26	
$\nu_4+\nu_3$	25.37	2.3162	4317.	2.3178		2.32	
	.71	2.3470	4261.				
$\nu_1$	.97	2.3704	4219.	2.3714		2.37	
	26.23	2.3935	4178.				
$\nu_2+2\nu_4$	26.57	2.4238	4126.	2.4262		2.42	
$\nu_3$				3.3185			
$\nu_4$				7.87			

lengths of the band centers are given in Table III, along with the wave-lengths as measured by Cooley<sup>1</sup> and Ellis.<sup>2</sup> In the latter table are also shown the classification given by Dennison<sup>6</sup> of the bands measured by Cooley and the classification made by Ellis of the bands which he had measured. The symbols indicate whether the bands are fundamental frequencies, harmonics of the fundamental frequencies, or some combination of the fundamentals or harmonics.

The  $2.3\mu$  region is shown in Fig. 1A to consist of a number of overlapping vibration-rotation bands. The four stronger ones are the bands observed by Cooley and Ellis. There appear to be three weaker ones, one of which was observed by Ellis. The  $2.2\mu$  band is the only one sufficiently separated from the neighboring bands to exhibit unconfused fine structure. The symmetry of the *P* and *R* branches is destroyed by the general increase of absorption with increase of wave-length. The *Q* branch is deep and sharp. It does not appear to spread out more to one side than to the other which indicates absence of perturbation between the rotation and vibration giving rise to the band. Perturbation, if present, would cause convergence of the *P* and *R* branches; that is, it would cause the frequency difference of the lines to become smaller in the direction of decreasing wave-length. Not enough lines are available for measurement to apply this test of convergence to this band. Quantum numbers are assigned to the lines from  $m = 5$  to  $m = -9$ , the num-

ber  $m$  referring to the initial state giving rise to the line. The average value of  $\Delta\nu$  for these lines has the value  $\Delta\nu = 10.7 \text{ cm}^{-1}$ . The moment of inertia computed from the equation  $I = h/4\pi^2\Delta\nu$  gives  $I = 5.17 \times 10^{-40}$  c.g.s. units.

At the  $2.316\mu$  band and the  $2.370\mu$  band, the  $Q$  branches are very sharp on the short wave side but shade off in the direction of increasing wave-length. This is very definite evidence of perturbation between the vibration and rotation to which the bands are due. All these bands overlap with so much confusion that it is impossible to assign quantum numbers to the lines or to determine the average frequency difference.

A number of bands were found in the first order spectrum of the  $1.6\mu$  region. The band at  $1.665\mu$  is strong and sharp, as can be seen in Fig. 1B. The

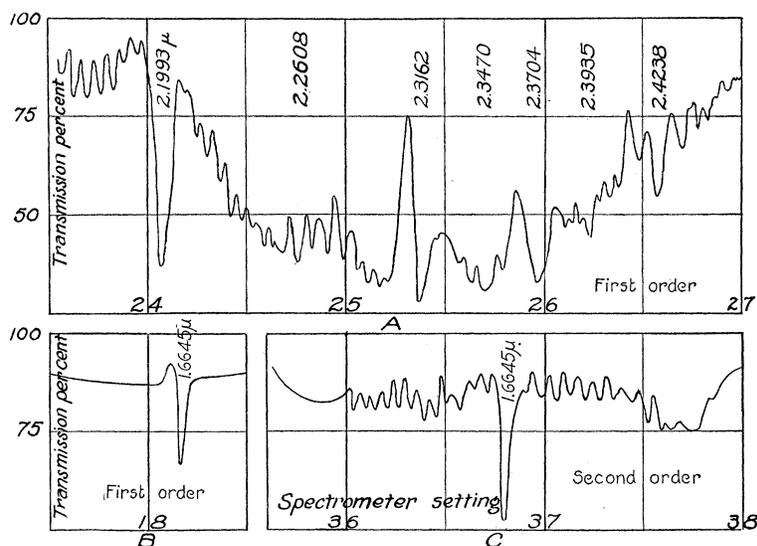


Fig. 1. Methane bands.

other bands of the first order are not very intense, but repeated observations proved them to be genuine. The fine structure was not resolved in the first order spectrum. In Fig. 1C is shown the second order spectrum of the  $1.665\mu$  band. The  $Q$  branch is very steep on the shorter wave-length side, but shades off on the long wave-length side, overlapping and concealing the first rotation band. This overlapping indicates perturbation. The irregularity in the shape of the band is due to the overlapping of other methane bands and of water vapor bands. The lines are in the main evenly spaced. The average frequency difference gives a value of  $\Delta\nu = 10.4 \text{ cm}^{-1}$ . The moment of inertia computed from this, by the formula already given, is  $I = 5.32 \times 10^{-40}$  c.g.s. units.

Table IV gives the average frequency difference and the resulting moments of inertia for the two bands measured by the author, and also the results given by Cooley for the three bands measured by him. The bands at  $1.66\mu$ ,  $2.2\mu$ , and at  $3.31\mu$  give values for the moment of inertia all of the same

order of magnitude. It is not probable that experimental errors account for all the variation in these values, but that they indicate slightly different moments of inertia, due either to lack of symmetry of the molecule, or to displacement of the atoms by vibration. Dennison<sup>6</sup> proposed an explanation of

TABLE IV. *Methane bands. Frequency difference and moment of inertia.*

Band $\mu$	Cooley Frequency cm <sup>-1</sup>	Moment of inertia c.g.s. units	Moorhead Frequency difference cm <sup>-1</sup>	Moment of inertia c.g.s. units
1.66			10.4	$5.32 \times 10^{-40}$
2.20			10.7	5.17
3.31	9.77	$5.66 \times 10^{-40}$		
3.5	15.3	3.61		
7.67	5.41	10.2		

the fact that the spacing of the  $7.7\mu$  band is about half that of the  $3.3\mu$  band, by assuming the overlapping of two bands, each having spacing equal to that of the  $3.3\mu$  band. Guillemin<sup>6</sup> considered Dennison's explanation improbable, since twice the frequency difference of the  $7.7\mu$  band differs from the frequency difference of the  $3.3\mu$  band by more than the probable experimental error. Also the entirely different spacing of the weak band at  $3.5\mu$  has not been accounted for on the basis of the symmetrical methane molecule. While the question of the three entirely different moments of inertia indicated by the three different spacings remain unsolved, it is significant that the spacing of the two bands measured by the author is close to the value measured by Cooley at the  $3.3\mu$  band.

The author acknowledges his indebtedness to Northwestern University for the use of its facilities and to Professor B. J. Spence, who suggested the problem.